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Molten salt/liquid metal extraction: Electrochemical determination of activity coefficients in liquid metals

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Abstract

The separation of fission products from a molten salt with a liquid metal has been largely investigated. However, it appears that the metals are not optimized for this purpose. The activity coefficients are needed for the simulations of the efficiency and selectivity of the extraction process which allows identifying the best suited extracting metal. The aim of this work is to find an easy way of determining the activity coefficients in liquid metals by means of electrochemical techniques. This paper describes the methods used as well as the results obtained.

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1. Introduction

The Thorium molten salt reactor (TMSR) concept is one of the six concepts which were selected as a possible concept for the IVth generation of nuclear energy systems. The fuel consists of ^{232}Th and ^{233}U solvated in a fluoride liquid mixture. Fission products, especially lanthanides, must be extracted in order to avoid any significant loss of neutrons and to let the TMSR reach a conversion ratio higher than unity. This may be achieved either by extracting the fission products from the molten salt mixture into a solvent liquid metal, or by selective oxide precipitation, or by fluorination, etc. The separation of fission products with a liquid metal, especially Bi, was investigated in the 1960s at Oak Ridge National Laboratory in the USA. However, it appears that the extracting metal was not optimized for this purpose [1].

The general reaction which occurs during a molten salt /liquid metal extraction follows the relationship:

$$\mathrm{MX}_y + y/z\mathrm{R} = \mathrm{M} + y/z\mathrm{RX}_z. \tag{1}$$

In this relation, M stands for a lanthanide or an actinide, X is chlorine or fluorine depending on what kind of salt is being used and R is a chemical metallic reductant. In this equation MX_y and RX_z are dissolved in the molten salt, whereas R and M are dissolved in the liquid metal. From the general reaction the equilibrium constant may be written as follows:

$$K = \frac{a_{\mathrm{M}} a_{\mathrm{RX}_z}^{y/z}}{a_{\mathrm{MX}_y} a_{\mathrm{R}}^{y/z}}. \tag{2}$$

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In this relation, a_i is the activity of the compound i. This activity may be described by the following relation $a_i = \gamma_i x_i$, where γ_i and x_i are respectively the activity coefficient and mole fraction for i. The distribution coefficients D_M for M and D_R for R are determined by introducing the activity coefficients and the mole fractions into the relation (2).

$$\log D_M = \frac{y}{z}\log D_R + \log K + \log\left(\frac{\gamma_{MX_y}\gamma_R^{y/z}}{\gamma_M\gamma_{RX_z}^{y/z}}\right), \quad (3)$$

where D_M and D_R are:

$$D_M = \frac{x_M}{x_{MX_y}}; \quad D_R = \frac{x_R}{x_{RX_z}}. \quad (4)$$

The γ_{MF_y} values in a fluoride molten salt are generally ranges from 1 to 10 whereas γ_{Li}^{y} and $\gamma_{M(Bi)}$ values vary between 10^{-14} and 10^{-6}. From relation (3) it can be seen that the outcome of the extraction depends on the values of the activity coefficients of the different compounds to be extracted both in the molten salt and in the liquid metal. Especially, the choice of the liquid metal is of primary importance.

A lot of data on activity coefficients are available in the literature [2]; these were used to determine candidate metals with low melting points (Al, Sb, Ga and Pb) [1].

2. Principle of activity coefficient measurements

The classical way of measuring activity coefficients is to construct a concentration cell as shown in Fig. 1.

On the left side, the electrode consists of the pure metal M under study. On the right side, the electrode is formed by the extracting solvent metal SM containing the metal M at a given concentration (M_{SM}). The electrolyte is constituted of a molten salt containing M in the form of dissolved MX_y at a fixed concentration.

The activity coefficient is simply determined by measuring the e.m.f. ΔE of the concentration cell which is connected to $\log\gamma_M$ by the following equation:

$$\log\gamma_M = \frac{-yF\Delta E}{2.3RT} - \log x_M \quad (5)$$

in which y stands for the number of electrons, F for the Faraday's constant, R for the ideal gas constant and T for the temperature. Eq. (5) shows that $\log\gamma_M$ is a function of the logarithm of the mole fraction x of M in the solvent metal and so it may easily derived from the variation ΔE as a function of $\log x_M$.

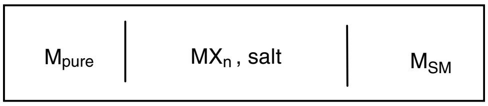

Fig. 1. A schematic presentation of a concentration cell for measuring activity coefficients.

This technique requires the pure metal M. This can be achieved by two methods: (i) use of pure M metallic rod; (ii) in situ deposition of pure M metal. The first one guaranties a(M) = 1, whereas the later avoids the use of the pure metallic rod (difficult for actinides). For reasons of convenience ΔE was obtained in this work from the measurements of the potentials of the M and M_{SM} electrodes versus the same experimental reference electrode.

3. Experimental

In order to establish a protocol for the activity coefficient measurements by means of electrochemical techniques, the study of the solvation properties of gallium with respect to gadolinium is presented in this paper. Gallium was chosen because of its low melting point, allowing the use of borosilicate glass and gadolinium because it has only two oxidation states (0 and III).

The electrochemical experiments were performed with a Princeton Applied Research potentiostat/galvanostat of the 263A model connected to a computer. The counter electrode and the inert working electrode were a W rod (diameter = 1 mm) introduced into a glass tube, leaving 1 cm of the rod uncovered on both sides of the tube. To validate the potentials obtained from the Gd electrodepot on the inert electrode of W, a 99.9 + % Gd rod (diameter = 6.35 mm, height = 50 mm) was fixed on an aluminium rod and immersed in the melt, as a working electrode, only for the time needed to obtain a stable potential. The reference electrode was an Ag rod (diameter = 1 mm) introduced into a borosilicate glass tube (open only on one side) which contained 50 mol% NaCl 50 mol% $CaCl_2$ + 0.67 mol/kg AgCl. All potentials are given versus this reference. The liquid working electrode (the solvent metal) was 10 g of 99.999% Ga that was put into a small cylindrical container (diameter = 2 cm, height = 2 cm) of borosilicate glass in which the contact was assured by a W rod in the bottom of the container leading out of the reactor in a glass tube isolated from the melt.

The salt used was a 100 g eutectic mixture of 50 mol% NaCl–50 mol% $CaCl_2$ prepared from pro analysis NaCl and 97% $CaCl_2$. The salt was put into a 150 ml borosilicate glass container and introduced into an electrochemical quartz reactor. Then the reactor was heated in an electrical furnace until the working temperature was reached, constantly under an argon atmosphere (the molten salt temperature was 530 °C). The molten salt was purified from oxygen by bubbling HCl(g) in the melt for 10 min, after which pO^{2-} = 4. The experiment was done by the following procedure:

1. Dissolution of 2 g of $GdCl_3$ in the melt.
2. Measurement of the equilibrium potential of Gd: (i) by using a pure Gd rod; (ii) by using different electrochemical techniques for the in situ Gd deposition.
3. Electrodeposition of Gd in the liquid Ga and measurement of the equilibrium potential.
4. Chemical analysis of the Ga sample by ICPMS.

The number (n) of moles of Gd extracted into the liquid Ga was derived from the amount of electricity (Q) passed during the electrolysis ($Q = ynF$), supposing the faradic effectiveness to be 100%.

4. Results and discussion

4.1. Potential measurements for the M electrode

During this work several electrochemical techniques (potentiostatic, galvanostatic, potentiodynamic and galvanodynamic) were tested in order to obtain pure deposited Gd. Hence, it became clear that the galvanodynamic experiment was probably the best adapted method for measuring the equilibrium potential for Gd metal on an inert electrode of W. Therefore only the results obtained by this technique are presented in this paper. The current was swept slowly (0.1 mA/s) from 0 to −0.03 A, back to 0 and continued to 0.03. The potential for pure Gd metal can be measured directly at $i = 0$ and the potential for $Cl_2(g)$ can be calculated from the plateau observed on the positive side. Fig. 2 shows a typical galvanodynamic experiment, from which it is possible to directly determine the equilibrium potential at $i = 0$ which was found to be equal to −1.985 V.

At the end of this type of experiment, in order to verify the value obtained for the equilibrium potential for pure Gd, a pure Gd rod was immersed in the melt and the potential measured was −1.985 V confirming the validity of the galvanodynamic technique.

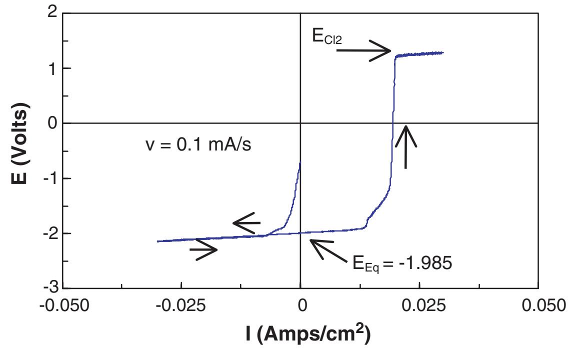

Fig. 2. Galvanodynamic experiment on W in eutectic NaCl–$CaCl_2 + 10^{-2}$ (mole fraction) $GdCl_3$ at 530 °C.

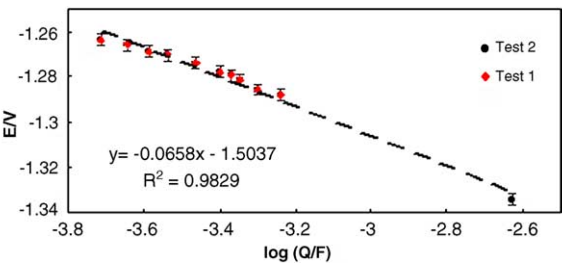

Fig. 3. Logarithm of the amount of electricity (Q) passed during the electrolysis divided by the constant of Faraday (F) as a function of potential (E) at 530 °C.

4.2. Potential measurements for the M_{SM} electrode

The next step was to determine the equilibrium potentials for the M_{SM} electrode by repeating electrolysis on the liquid Ga in order to introduce Gd into the liquid metal (W as the counter electrode).

The results are presented in Fig. 3. This figure shows the values of the logarithm of the amount of electricity (Q) passed during the electrolysis divided by the constant of Faraday as a function of the potential of the M_{SM} electrode (the sensitivity of the potentiostat in open potential circuits is ±2 mV). This allowed us to verify the number of electrons used in the electrochemical reaction during the electrolysis. The diamond like points corresponds to an experiment with a higher concentration of $GdCl_3$ in melt than the one relative to the last point. In the later case, the potential was corrected in order to take into account the difference in concentrations.

It can be remarked that all the points are aligned on a straight line whose slope is very close to the theoretical one for three electrons (theoretical: 0.053; experimental: 0.066). This was later confirmed by analysing the sample by ICPMS after the end of the experiment: the 10 g Ga sample contained 7.366 mol Gd which correspond to $\log(Q/F) = -2.66$ whereas the electrolysis calculations gave a $\log(Q/F) = -2.63$.

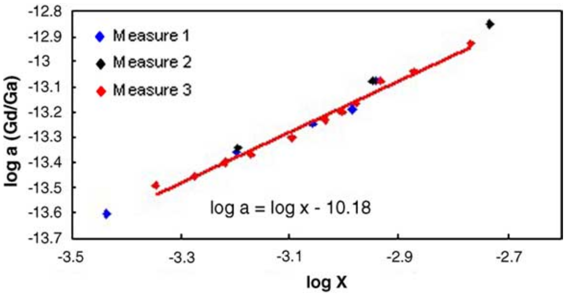

Fig. 4. Logarithm of the mole fraction of Gd in Ga as a function of the logarithm of the activity of Gd in Ga at 530 °C.

4.3. Activity coefficients calculations

The results are presented in Fig. 4 for three different experiments. These experiments are in good agreement and lead to a unique activity coefficient equal to $\gamma_{\mathrm{Gd}} = 10^{-10.18\pm0.02}$. This logarithm of γ_{Gd} (proportional to the solvation energy of Gd in Ga) is slightly different (6%) from the value reported in the literature ($\gamma_{\mathrm{Gd}} = 10^{-9.55}$) [3].

5. Conclusions

This work was conducted with the aim to develop a protocol for measuring activity coefficient for different elements in liquid metals by means of electrochemical methods. This was developed for Gd in Ga at 530 °C for different concentrations of Gd in Ga from 0.04 to 0.2 mol%. The results obtained by depositing Gd on W were verified by using pure Gd metal to measure the equilibrium potential for an activity considered to be 1. Moreover, ICPMS analysis of a Ga sample confirmed a 100% effectiveness of the electrodeposition of Gd in Ga. A slight difference was encountered when comparing the activity coefficient measured to the only one reported in the literature. This difference could be explained by the domains of concentrations studied in our work and in that of Kober (0.34 mol%) [3]. This will be studied later on.

Further works will be carried out in order to determine the temperature dependence of the activity coefficient of gadolinium and later on other lanthanides solvent metals systems.

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